JOURNAL OF MATERIALS SCIENCE 24 (1989) 2275–2280

Preparation of ultrafine zirconium dioxide particles by thermal decomposition of zirconium alkoxide vapour

MOTOAKI ADACHI
Radiation Center of Osaka Prefecture, Sinke-cho, Sakai 593, Japan

KIKUO OKUYAMA*, SEONGWON MOON, NOBORU TOHGE‡,
YASUO KOUSAKA
Department of Chemical Engineering, and ‡Department of Applied Chemistry,
University of Osaka Prefecture, Sakai 591, Japan

Ultrafine zirconia particles are produced by thermal decomposition of zirconium tetratertiary butoxide (ZrTB) vapour. The introduction of ZrTB vapour into the cylindrical electric furnace, is achieved by three different methods: (evaporator, pressurized nebulizer and ultrasonic nebulizer). The properties of the fine particles obtained by these methods are mainly analysed by X-ray diffraction and transmission electron microscopy. It is found that ultrafine zirconia particles produced at relatively low temperatures from 600 to 700° C are spherical in the diameter range 0.035 to 0.15 μm and of tetragonal phase. Furthermore, two-component fine particles of zirconia–silver are generated by putting the silver solid inside the furnace containing alkoxide vapour, and are deposited by inertia on to a glass substrate under low pressure to form films having a thickness of 17 to 33 μm. The electrical characteristics of the films are evaluated, and the conductance of the film is found to increase with the content of the silver component.

---

1. Introduction

Zirconia powders have become increasingly important in a number of high-technology industries, and are of interest as raw materials for ceramics. As an ideal powder for new ceramics, high-purity, uniformly sized, spherical, and unagglomerated fine particles are required. In most previous investigations, preparation of zirconia powders has been limited to liquid-phase chemical reaction. Zirconia powder production from gaseous precursors has been reported in some studies where the particles were prepared by injecting the zirconium metal powder into the plasma arc devices [1–3] and by the chemical reactions of zirconium chloride vapour and zirconium alkoxide vapour [4, 5]. Recently, some metal oxide powders, e.g. TiO_2, SiO_2 and Al_2O_3 have been prepared from their alkoxide vapours by chemical vapour deposition (CVD), because high-purity particles of controlled crystalline structure can be produced from alkoxide vapours at a relatively low temperature. However, the preparation of zirconia from zirconium alkoxide vapour has only been studied by Mazdiyasni *et al.* [5]. Although they prepared the zirconia particles by the thermal decomposition of zirconium butoxide, the particles were amorphous, of very wide particle-size distribution, and nonspherical. It is not clear how the phase transformation depends on reaction temperature. In addition, ultrafine particles below about 0.1 μm diameter are of interest and considerable effort is being expended to produce ultrafine powders of zirconium dioxide, because sintering becomes possible at lower temperatures. Accordingly, the production of ultrafine spherical and crystalline zirconia powders with narrow size distribution has been greatly expected, by chemical vapour deposition of zirconium alkoxide.

In this paper, the production of zirconium oxide particles by the thermal decomposition of zirconium tetratertiary butoxide (ZrTB) vapour is developed to produce high-purity, ultrafine and spherical zirconia particles using an electric furnace. In the experiments, the effects of generation method of alkoxide vapour, initial vapour concentration and reaction temperature on the properties of fine zirconia powders in gas-phase chemical reactions were examined. The generated particles were collected and analysed by transmission electron microscopy (TEM), X-ray diffraction (XRD), and photon correlation spectroscopy. Furthermore, two-component particles of zirconia–silver were prepared by mixing the silver vapour with zirconia vapour and particles in the furnace, and were deposited

---

*Author to whom all correspondence should be addressed.

0022–2461/89 $03.00 + .12

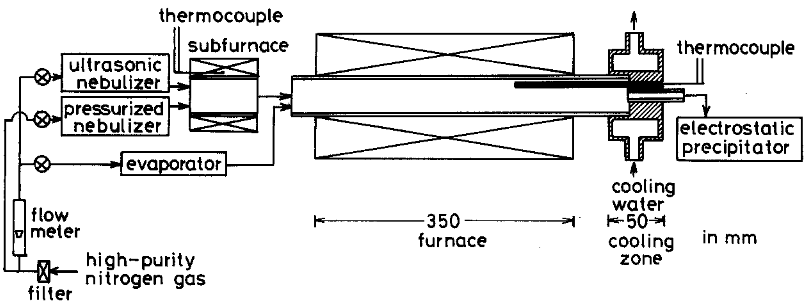

Figure 1 Experimental system for producing zirconia particles.

on the glass substrate by inertial impaction under vacuum in order to form a film. The electrical characteristics of this film are evaluated.

2. Zirconia particle production experiment

Fig. 1 shows a schematic drawing of the experimental apparatus used in this study. To generate zirconium tetratertiary butoxide (ZrTB) vapour, the following three different methods, by which the ZrTB is supplied to the furnace, were used: (a) the evaporator, where ZrTB liquid is vaporized by the heater and the vapour is carried out by nitrogen gas; (b) the pressurized nebulizer; and (c) the ultrasonic nebulizer, by which droplets of ZrTB are generated. The ZrTB vapour was thermally decomposed in the furnace to produce supersaturated zirconium dioxide vapour. The particles generated by thermal decomposition were collected using an electrostatic precipitator in order to analyse their shape and crystal structure by electron microscopy and X-ray diffraction. Particle-size distributions were measured by dynamic laser light scattering (photon correlation spectroscopy) using System 4700-PS/MW (Malvern Co. Ltd).

2.1. Evaporator method

As shown in Fig. 1, the generation method using an evaporator consists of three sections: the evaporator, the furnace and the cooling section. The ZrTB liquid was maintained in a heated glass container that served as the vapour source. Clean nitrogen gas was passed through the evaporator, and left saturated with the ZrTB vapour. The temperature of the evaporator was kept at 280° C by the thermocontroller. The ZrTB vapour thus obtained was continuously introduced into a reactor furnace 35 cm long and 24 mm diameter, at a flow rate of $2\,\mathrm{l\,min^{-1}}$. This furnace was also maintained between 550 and 1080° C by the thermocontroller. The ZrTB vapour was thermally decomposed to produce supersaturated zirconia vapour according to the following reaction

$$\mathrm{Zr(OBu^t)_4} \rightarrow \mathrm{ZrO_2} + 2\,\mathrm{Bu^tOH} + \text{olefin}$$

When ZrTB vapour is thermally decomposed according to the above reaction, zirconia, butanol and olefin are produced in successive steps.

The ZrTB vapour reacts sensitively with water vapour or oxygen gas, therefore the nitrogen gas was passed through a drying column (containing silicagel, calcium sulphate, active anhydrous and magnesium perchlorate) and a deoxidizer (containing activated copper) to obtain dry and oxygen-free carrier gas. Thus, water and oxygen concentrations in the nitrogen gas were less than 1.0 p.p.m. The nitrogen gas supply was regulated by a pressure regulator, cleaned by filters, and metered and delivered to the evaporator. If a sufficient level of supersaturation of zirconia vapour was attained, ultrafine primary zirconia clusters were produced by homogeneous nucleation. Larger secondary particles were formed by the agglomeration of clusters and by the simultaneous heterogeneous condensation of vapour molecules on the clusters.

Fig. 2 shows the temperature distributions of the reactor furnace for different operating temperatures. These temperature profiles were measured at the centre of the furnace by inserting a thermocouple. It was found that temperatures tended to increase and decrease almost symmetrically up and down the furnace. Because the temperature has a maximum around the centre of the furnace, the maximum temperature was used to denote the experimental results.

Fig. 3 shows X-ray diffraction patterns of the generated zirconia particles under various furnace temperatures. Temperature of the evaporator was maintained at 280° C, and the flow rate of nitrogen gas was $2\,\mathrm{l\,min^{-1}}$. From the patterns for particles generated at the maximum furnace temperatures of 660, 760 and 1080° C, these particles were found to be tetragonal zirconia (t-$\mathrm{ZrO_2}$).

When the t-$\mathrm{ZrO_2}$ particles prepared at 1080° C were reheated at 900° C for 1 h, they changed to monoclinic zirconia (m-$\mathrm{ZrO_2}$). However, those left at room temperature for three months showed no change in crystal structure. The particles generated at 550° C were

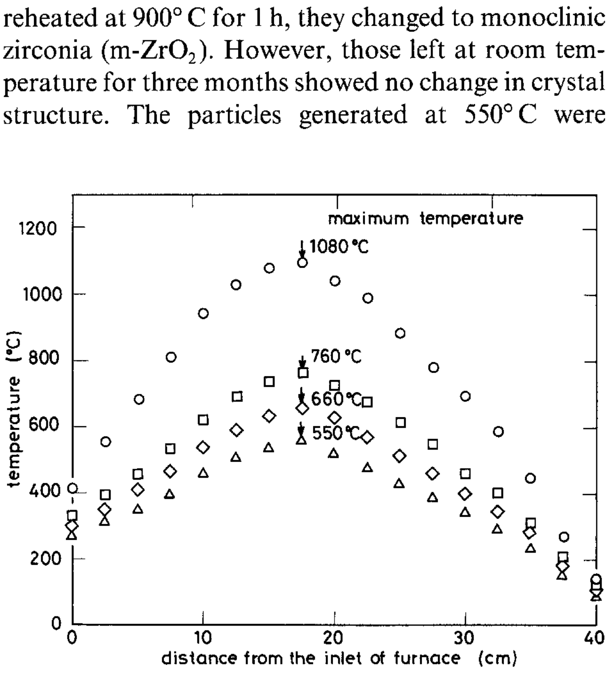

Figure 2 Temperature profile inside the furnace. Flow rate $2\,\mathrm{l\,min^{-1}}$.

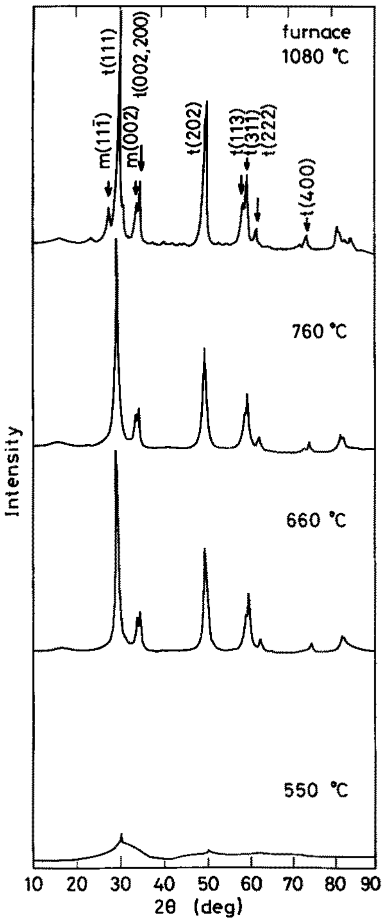

Figure 3 X-ray diffraction patterns of zirconia particles generated using the evaporator at various furnace temperatures. Evaporator temperature 280° C, flow rate 2 l min^{-1}.

found to be amorphous, having the two distinctive peaks of *t*-ZrO$_2$. Thus the t-ZrO$_2$ was found to be directly generated under relatively low temperatures by this method.

The interest in t-ZrO$_2$ particles has increased considerably with the discovery of transformation toughening [6–8], which is important in the engineering ceramics. Generally, the t-ZrO$_2$ is stable between 1170 and 2370° C, and m-ZrO$_2$ appears below 1170° C. It has been reported that a tetragonal–monoclinic phase transformation occurs at 1170° C. It appears that ZrO$_2$ powder can, under certain circumstances, exist metastably at temperatures below 1170° C with cubic or tetragonal phases [1, 5, 9, 10]. These powders have the common characteristic of particle sizes lower than 0.1 μm. Our powder may also be generated by the same mechanisms as those mentioned above. However, the formation and metastability of these ultrafine powders is not well understood and may involve either surface energy or chemical effects [1, 10–12].

Fig. 4 shows transmission electron micrographs of fine particles produced under temperatures of 550, 660, 760 and 1080° C. On comparison of these photographs, it is seen that the particle size decreases on increasing the furnace temperature from 550 to 760° C, and increases on increasing the temperature from 760 to 1080° C because of the agglomeration of fine particles. The particles produced at 760° C are spherical and of uniform size ($\sim$0.05 μm).

Fig. 5 shows the particle size distributions measured by photon correlation spectroscopy as a function of furnace temperature. We note that the particle size

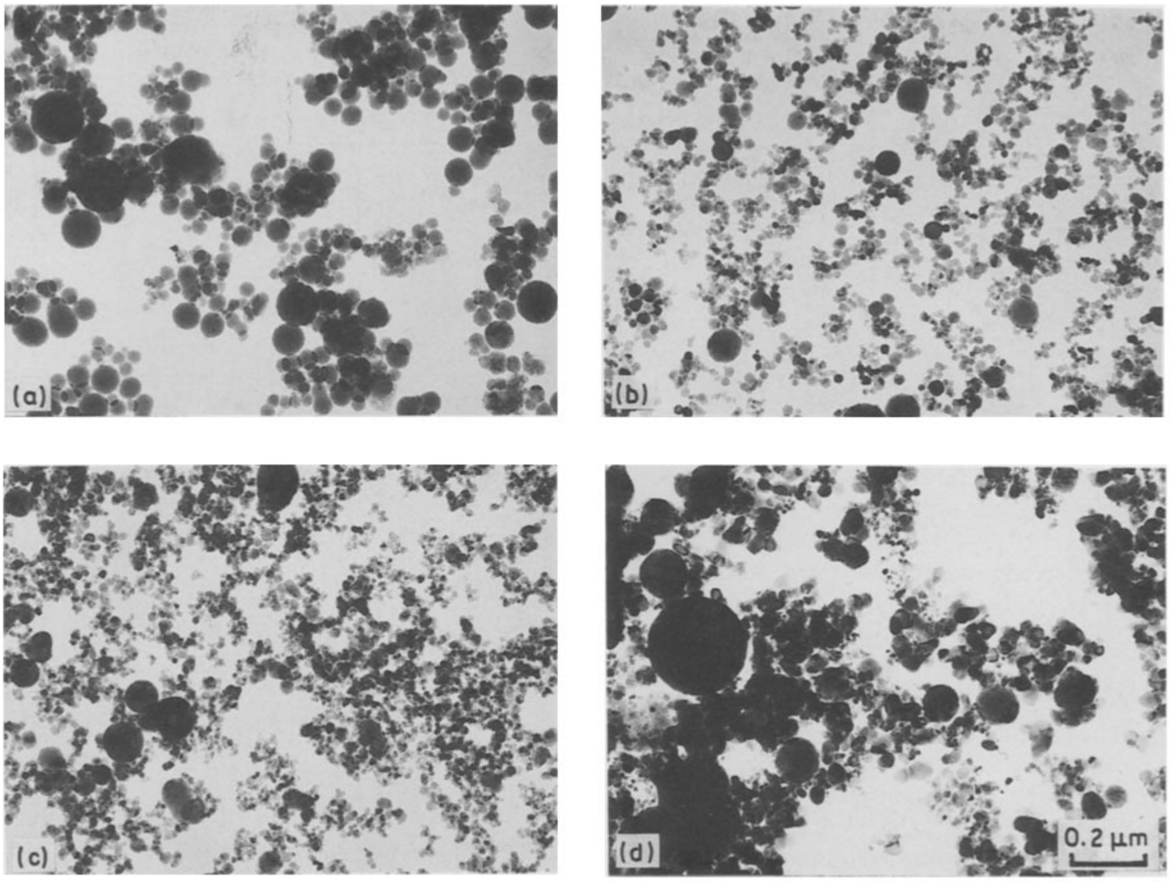

Figure 4 Transmission electron micrographs of fine zirconia particles generated using the evaporator at furnace temperatures of (a) 550° C, (b) 660° C, (c) 760° C, (d) 1080° C.

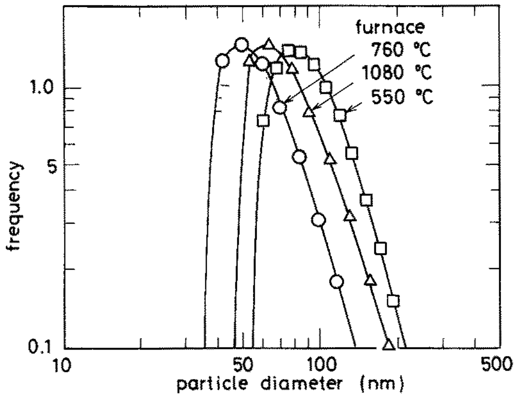

Figure 5 Change in size distribution of ZrO_2 particles with reaction temperature. (□) $d_{pg} = 92.7$ nm, $\sigma_g = 1.36$, (○) $d_{pg} = 60.3$ nm, $\sigma_g = 1.38$, (△) $d_{pg} = 78.3$ nm, $\sigma_g = 1.40$. Evaporator temperature 280° C, flow rate $2\,l\,min^{-1}$.

distributions of particles are less than about 200 nm, indicating a similar tendency to that seen in the electron micrographs. The smallest ZrO_2 particles are produced at a furnace temperature of 76° C. Their geometric mean diameter, d_{pg}, and geometric standard deviation, σ_g, are 60.3 nm and 1.38, respectively.

Fig. 6 shows the time-dependent changes in the weight of particles produced by the generator using the evaporator, the pressurized nebulizer and the ultrasonic nebulizer. The ordinate is the weight of powder captured during 5 min by the electrostatic precipitator. The weights of powder generated by the evaporator (shown by open circles) decrease slightly with time, because zirconium alkoxide begins to polymerize at the boiling point (190 to 210° C). This polymerization obstructs the continuous and constant production of zirconia particles, because the polymeric compounds have a lower vapour pressure. Therefore, the pressurized nebulizer or ultrasonic nebulizer is used instead of the evaporator.

2.2. Pressurized nebulizer and ultrasonic nebulizer methods

When the pressurized nebulizer and ultrasonic nebulizer are used, the generation system consists of four sections; the pressurized nebulizer or ultrasonic nebulizer, sub-furnace, reactor furnace, and cooling section. The ZrTB droplets generated by the pressurized nebulizer or ultrasonic nebulizer were introduced into the sub-furnace of 12 cm length and 13 mm diameter to be vaporized at 280° C. The vapour thus generated was supplied to the reactor furnace maintained at 550 to 1080° C. In the experiment using the pressurized nebulizer, a solution of ZrTB diluted with the dry ethanol in an equal volume ($1.19\,mol\,l^{-1}$) was used, because the original ZrTB liquid could not be nebulized because of its high viscosity. When the ethanol solution containing $1.19\,mol\,l^{-1}$ of ZrTB was nebulized at the flow rate of $3.8\,l\,min^{-1}$, the ZrTB vapour supplied to the reactor furnace was $1.91 \times 10^{-4}\,mol\,min^{-1}$. In the use of the ultrasonic nebulizer, the solution containing $0.59\,mol\,l^{-1}$ ZrTB was nebulized. The ultrasonic nebulizer (Model NE-U11B, Tateishi Electric Co. Ltd) can generate ultrasonic waves of 1.7 MHz. Using this nebulizer, the ethanol solution of ZrTB, in which the concentration is lower than $0.59\,mol\,l^{-1}$, could be nebulized. When the flow rate of carrier gas was $2\,l\,min^{-1}$, the ZrTB vapour was supplied to the reactor furnace at $3.54 \times 10^{-3}\,mol\,min^{-1}$.

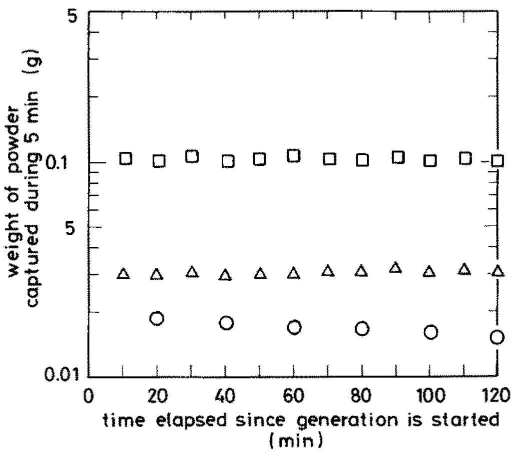

Figure 6 Time-dependent change in the captured weight of zirconia powder generated using (○) the evaporator, (△) the pressurized nebulizer and (□) the ultrasonic nebulizer.

Time-dependent changes in the weight of particles produced by both nebulizers are shown in Fig. 6. In these experiments, the reactor furnace was maintained at 760° C and the ethanol solution of ZrTB the flow rate, and the subfurnace temperature were kept at the above values. The weights of particles generated by the ultrasonic nebulizer and the pressurized nebulizer were kept at about 0.1 and 0.03 g, respectively, within 2 h. In the case of an operating time longer than 2 h, the generation of particles decreased, because the number of droplets nebulized depends on the level of liquid in the nebulizers. This decrease can be improved by maintaining a constant level of ZrTB liquid in both nebulizers. Because the vapour content of alkoxide supplied by the ultrasonic nebulizer was larger than that by the pressurized nebulizer, the amount of powder generated by the ultrasonic nebulizer was larger than that generated by the pressurized nebulizer.

In the case of the pressurized nebulizer, the yield, that is, the percentage conversion of ZrTB to the zirconia particles, was about 20%.

From X-ray diffraction results of particles generated using the pressurized and ultrasonic nebulizers, it was seen that the zirconia particles generated have tetragonal phase as shown in the results obtained by evaporator method. The amorphous particles generated at 550° C were also transformed to the tetragonal phase between 550 and 760° C.

From the electron micrographs, it was found that the change in particle size with temperature of the reactor furnace had a similar tendency as in the results obtained by the evaporator method. In addition, it was found that particles generated using the ultrasonic nebulizer have a larger size than those generated using the pressurized nebulizer. This difference is due to the amount of ZrTB vapour supplied by the ultrasonic nebulizer per unit time ($3.54 \times 10^{-3}\,mol\,min^{-1}$)

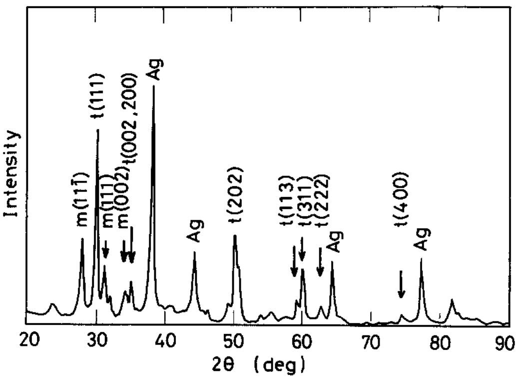

Figure 7 X-ray diffraction pattern of the zirconia–silver particles. Furnace temperature 1250° C, evaporator temperature 280° C, flow rate $2\,l\,\text{min}^{-1}$.

being larger than that supplied by the pressurized nebulizer ($1.91 \times 10^{-4}\,\text{mol}\,\text{min}^{-1}$).

3. Preparation of thin films by deposition of zirconia–silver particles

In the generation of zirconia-silver particles, the generator using the evaporator as shown in Fig. 1 was used. The silver powder (99.9% purity) contained in the ceramic boat was placed in the centre of the reactor furnace. The furnace was operated at 1100 and 1200° C to generate a sufficient amount of silver vapour. The silver vapour thus generated was introduced into the cooling section together with the zirconia particles generated by thermal decomposition, until supersaturation was attained. Accordingly, the supersaturated silver vapour deposited on the zirconia particles and the reactor walls.

Fig. 7 shows the X-ray diffraction pattern of the zirconia-silver particles generated at the maximum furnace temperature of 1200° C. The pattern indicates four major peaks for silver in addition to three major peaks for tetragonal zirconia. The percentage of silver in the zirconia–silver particle which was obtained from the calibration curve for the intensity ratio I_{Ag}/I_T (I_{Ag} and I_T are the intensities of the strongest peak for silver ($2\theta = 38$) and for tetragonal zirconia ($2\theta = 30$), respectively) was 28 wt %.

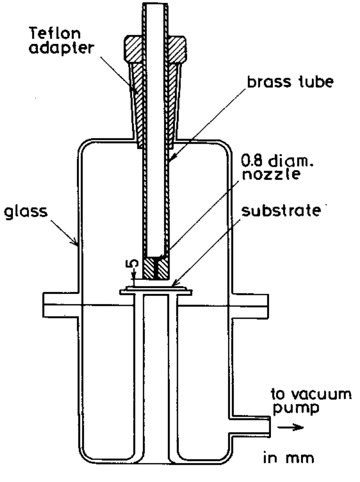

Figure 8 Deposition chamber for ultrafine particles.

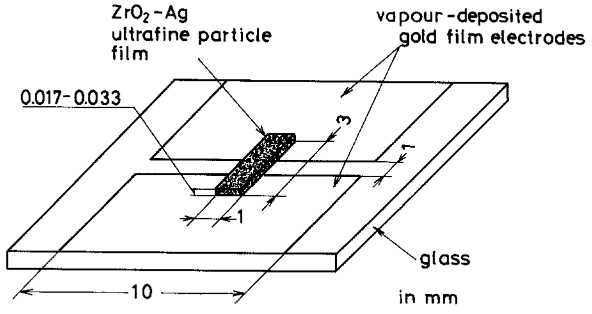

Figure 9 Zirconia–silver particle film.

Fig. 8 shows the deposition chamber used in the production of the ultrafine particle film [13]. Zirconia–silver particles were introduced through a critical nozzle to the deposition chamber which was pumped down to about 30 torr. Particles were accelerated to about $200\,\text{m}\,\text{sec}^{-1}$ at the critical nozzle and were then deposited on the glass substrate by inertial force to form the film.

Fig. 9 shows the zirconia–silver particle film. The glass substrate (Corning 7059) had two gold-plated electrodes with a gap between them of 1 mm. The ultrafine particles were deposited over the gap, so as to convert the two electrodes. The width and length of the film were 1 and 3 mm, respectively, and the thickness varied from 17 to 33 μm. The electrical current flowing through the produced film was measured by an electrometer in the high-purity nitrogen gas which was passed through a drying column and a deoxidizer, as described previously. The operating voltages were changed from 0 to 1000 V d.c. and the temperature of the film was maintained at 175° C.

Fig. 10 shows the voltage–current response of the zirconia–silver particle film. On the film produced by only zirconia particles, no electric current could be measured. The currents of the zirconia–silver particle

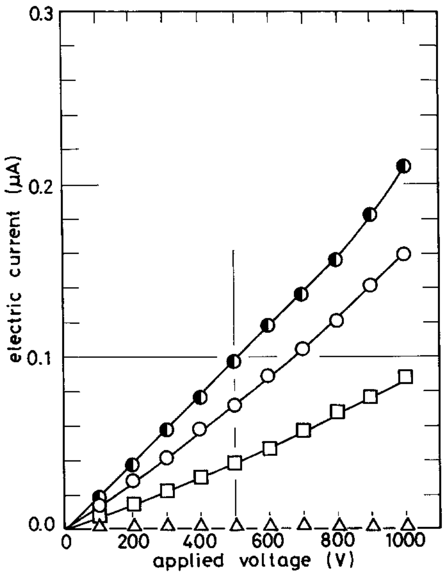

Figure 10 Voltage–current response of ZrO_2–Ag particle film. ZrO_2–Ag particles: (◐) furnace temperature 1200° C, film thickness 33 μm, (○) furnace temperature 1200° C, film thickness 19 μm, (□) furnace temperature 1100° C, film thickness 17 μm. ZrO_2 particles: (△) furnace temperature 1200° C, film thickness 18 μm. Substrate temperature 175° C, in dry nitrogen.

film were found to increase linearly with increasing voltage. This linearity may be inherent for the particle films as was also found in the particle film of tin dioxide by Adachi *et al.* [13]. The electric current of the film produced by the zirconia–silver particles at a furnace temperature of 1200° C was higher than that at 1100° C, because the vapour pressure of silver at 1200° C was sufficiently higher than that at 1100° C. The particle film having a thickness of 33 μm gave an electric current higher than that for a thickness of 19 μm. Therefore, the current was found to flow uniformly through the particle films. These results for film thickness and linearity of the current–voltage characteristic suggest that silver particles uniformly cover the zirconia particles.

4. Conclusions

The production of ultrafine zirconia particles has been studied by the thermal decomposition of zirconium butoxide vapour in a furnace, and the following conclusions have been drawn.

1. The size and crystal structure of zirconia particles obtained mainly depends on the furnace temperature. Zirconia particles having geometric mean diameters of about 60 nm, geometric standard deviations of 1.4, and tetragonal crystal structure can be obtained at furnace temperatures 600 to 700° C by thermal decomposition of ZrTB vapour. This temperature is very low compared with the usual phase-transformation temperature above 1170° C.

2. It is possible to produce zirconia particles stably and continually by the methods of evaporation, nebulizer and ultrasonic nebulizer. The size of zirconia particles also depends on the amount of alkoxide vapour introduced into the furnace indicating that the size of the zirconia particle becomes larger with the vapour concentration.

3. Two-component zirconia–silver particles were generated and deposited on a glass substrate by inertial impaction under vacuum in order to form a film. The electrical characteristics of this film depends on the amount of the silver component.

References

1. C. A. PICKLES and A. MCLEAN, *J. Ceram. Bull.* **62** (1983) 1004.
2. J. D. HOLMGREN, J. O. GIBSON and C. SHEER, *J. Electrochem. Soc.* **111** (1964) 362.
3. V. D. PARKHOMENKO and P. I. SOROKU, in Proceedings of the 5th International Symposium on Plasma Chemistry. (International Union of Pure and Applied Chemistry, 1981) p. 861.
4. M. FORMENTI, F. JUILLET, P. MERIAUDEAU, S. J. TEICHNER and P. VERGNON, *J. Colloid Interface Sci.* **39** (1972) 79.
5. K. S. MAZDIYASNI, C. T. LYNCH and J. S. SMITH, *J. Amer. Ceram. Soc.* **48** (1965) 372.
6. R. C. GARVIE, R. H. J. HANNINK and R. T. PASCOE, *Nature* **258** (1975) 703.
7. D. L. PORTER and A. H. HEUER, *J. Amer. Ceram. Soc.* **60** (1977) 183.
8. N. CLAUSSEN, *ibid.* **61** (1978) 85.
9. K. S. MAZDIYASNI, C. T. LYNCH and J. S. SMITH, *ibid.* **49** (1966) 286.
10. T. MITSUHASHI, M. ICHIHARA and U. TATSUKE, *ibid.* **57** (1974) 97.
11. R. C. GARVIE, *J. Phys. Chem.* **82** (1978) 218.
12. Y. MURASE and E. KATO, *J. Amer. Ceram. Soc.* **62** (1979) 527.
13. M. ADACHI, K. OKUYAMA, Y. KOUSAKA and H. TANAKA, *J. Aerosol. Sci.*, **19** (1988) 253.

Received 7 April
and accepted 5 September 1988